Original document

SOLUTION FOR FORMING WATER REPELLENT FILM

Patent number: JP11322368
Publication date: 1999-11-24
Inventor: AKAMATSU YOSHINORI; HAMAGUCHI SHIGEO
Applicant: CENTRAL GLASS CO LTD
Classification:
- international: C03C17/30; C09K3/18
- european:
Application number: JP19980132876 19980515
Priority number(s): JP19980132876 19980515

View INPADOC patent family

Report a data error here

Abstract of **JP11322368**

PROBLEM TO BE SOLVED: To obtain a film having high hardness, high adhesion and capable of keeping excellent water repellency for a long period together with durability and abrasion resistance by hydrolyzing a fluoroalkyl group-containing silane compound in the presence of an acid catalyst and forming unimolecular layer of monomer of the hydrolyzate on the surface of the substrate. SOLUTION: A fluoroalkyl group-containing silane compound comprising a fluoroalkyl-alkoxysilane compound of the formula CF3 (CF2)m (CH2)n SiR<1> x (OR<2>)3-x . [(m) is 0-15; (n) is 0-2; (x) is 0-2; (m+n)=0-17; R<1> and R<2> are each CH3 , C2 H5 or C3 H7] is mixed with a diluting solvent comprising the same kind of alcohol as the alkoxy group in the silane compound and about >=0.01 N acidic aqueous solution as a catalyst and the silane compound is subjected to hydrolysis reaction. The solution is applied onto a substrate such as glass substrate and a monomer which is hydrolyzate of the silane compound is subjected to condensation through dehydration reaction with silanol group of the glass to fix the monomer on the surface of the substrate. Then, the monomer is cured at a temp. of about 80-350 deg.C to form water-repellent film comprising transparent unimolecular layer excellent in durability.

CLAIMS

[Claim(s)]
[Claim 1] The base material characterized by forming the water-repellent coat which fixes the monomer of the hydrolyzate of the fluoro alkyl group content silane compound which the basis of an acid catalyst was made to hydrolyze on a base material front face, and consists of a monomolecular layer.
[Claim 2] The monomer of the hydrolyzate of the fluoro alkyl group content silane compound which the basis of an acid catalyst was made to hydrolyze is fixed on a base material front face. Are a solution for forming the water-repellent coat which consists of a monomolecular layer, and the solution containing this monomer makes concentration of a fluoro alkyl group content silane compound 0.1 - 15 % of the weight. And the solution for water-repellent coat formation characterized by being generated using the solution which used alcohol equal to the class of alkoxy group in this alkoxy group content silane compound as the diluent solvent, and made aqueous acids the catalyst.
[Claim 3] Said fluoro alkyl group content silane compound is a solution for water-repellent coat formation according to claim 2 characterized by being the fluoro alkyl alkoxysilane compound expressed with a general formula [1].
CF3(CF2)m(CH2)nSiR1x(OR2)3-x [1]
(Each integer of m=0-15, n=0-2, x=0-2, however m+n=0-17, R1, R2=CH3, C2H5, C3H5, and C4H7 are expressed among a formula)
[Claim 4] The hydrolyzate of a fluoro alkyl group content silane compound is a solution for water-repellent coat formation according to claim 2 to 3 characterized by consisting of 99.5% of the weight or more of a monomer.
[Claim 5] The formation approach of the water-repellent coat characterized by consisting of a process which applies the solution for water-repellent coat formation according to claim 2 to 4 to a base material front face, and a hardening process which fixes the fluoro alkyl group subsequently to this solution for water-repellent coat formation contained on this base material front face, and forms the water-repellent coat of a monomolecular layer.

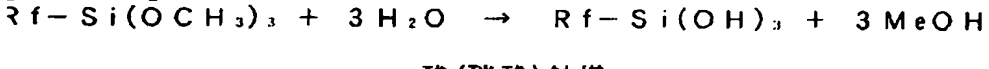
[Translation done.]

DETAILED DESCRIPTION

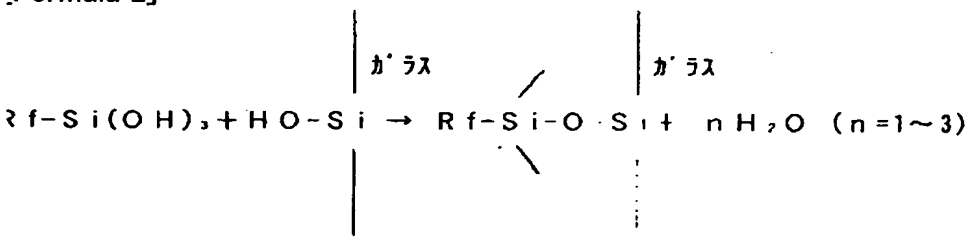
[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the base material in which the formation approach of the solution for forming a water-repellent coat in base material front faces, such as mirrors the various aperture material the object for construction, the object for automobiles, the object for vessels, for aircrafts, etc., the object for bathrooms, for automobiles, etc. and a glass substrate which can be used for the various transparence goods of various fields, such as industrial use, etc. further in addition to this, and a water-repellent coat, and this coat were formed.
[0002]
[Description of the Prior Art] Recently, it has more excellent endurance and water repellence, and a transparent water-repellent coat which maintains the outstanding water-repellent engine performance for a long time has been desired. In order to reply to these needs, it is necessary to consider as a water-repellent base material equipped with the water-repellent thin film which has high abrasion resistance (traverse-proof nature), for example.
[0003] Then, invention indicated to Japanese Patent Application No. No. (JP,9-132433,A) 294106 [seven to] for which these people already applied By forming in a glass front face the base film which has the unique and detailed toothing-like surface front face controlled by high specific surface area which was excellent in a high mechanical strength and endurance with the high degree of hardness, and forming the water-repellent film which covers this base film The deposit efficiency and adhesion of this water-repellent film are raised, and light-fast ability is made to improve further.
[0004] Moreover, invention indicated to Japanese Patent Application No. No. (JP,9-309746,A) 131595 [eight to] for which these people already applied It is supposed that a water-repellent membrane layer is formed in a glass substrate front face (detailed concave convex glass substrate front face which gave the crack of the shape of a muscle which has directivity depending on the case) in the condition that the temperature of a glass substrate is in about 90-200 degrees C in case the water-repellent film is formed on the surface of a glass substrate. Weatherability, abrasion resistance, the water-repellent engine performance which resembled abrasion-proof nature and endurance markedly, and was excellent in them is demonstrated.
[0005] For patent No. 2500178, moreover, as a water-repellent oil-repellent art on the front face of a base material The approach of forming a chemisorption monomolecular layer in base material front faces, such as a glass substrate, using the silane system compound containing two or more carbon fluoride radicals and Krol radicals is shown. The process immersed in the solution which dissolved the fluoro alkyl group content chlorosilicane compound in the solvent of a non-drainage system in a substrate, After taking out a base material, the process dried in the ambient atmosphere which is not included in a real target, excluding moisture at all is shown, and it is shown that the monomolecular layer formed in the base material front face demonstrates the outstanding abrasion resistance.
[0006]
[Problem(s) to be Solved by the Invention] Water-repellent glass which is the layer which is as complicated as the film configuration of the two-layer structure of the unique base film and the water-repellent film although the water-repellent glass of a Japanese Patent Application No. [No. 294106 / seven to] publication mentioned above can fully reply to the needs mentioned above, and does not need a simple and simple substrate layer, for example, and has high performance more is also just going to desire.
[0007] Moreover, since it is necessary to manage water-repellent glass given in Japanese Patent Application No. No. 131595 [eight to] etc. in the condition of having raised the workability at the time of manufacture, especially glass substrate temperature to 90-200 degrees C, it may be hard to say that the handling is simple enough and that it is efficient.
[0008] moreover, by the approach currently indicated by the water-repellent oil repellent agent on the front face of glass of a patent [No. 2500178] publication, extremely, to water, since reactivity is high, a chlorosilicane system compound needs to perform many processes under the environment without moisture dried extremely --

etc. -- handling is very troublesome.
[0009] That is, the thing in which the conventional monomolecular layer is made to form, and the thing in which the substrate film is made to form in order to raise endurance ability required complicated management conditions and a complicated process, had become cost quantity, and generally what does not have the substrate film on the other hand needed to be [the reactivity on a water repellent component and the front face of glass] inadequate, and they needed to deal with a reactant high compound like fluoro alkyl group content chlorosilicane in it.
[0010]
[Means for Solving the Problem] By making this invention in view of the technical problem which the former requires, and limiting the content of the fluoro alkyl group content silane compound in the solution for water-repellent coat formation, and the class of diluent solvent The obtained solution for water-repellent coat formation consists only of a monomer of the hydrolyzate of a fluoro alkyl group content silane compound. As for the water-repellent coat which applied this solution and was obtained, a monomolecular layer is formed, and these film is a high degree of hardness and high adhesion, and it has endurance and abrasion resistance. It is the base material in which the formation approach of a water-repellent coat with very easy actuation and this coat which find out having the water-repellent engine performance which was excellent in the long run, and do not need to deal with a reactant high compound while a substrate layer is unnecessary and can form membranes in ordinary temperature were formed.
[0011] That is, this invention fixes the monomer of the hydrolyzate of the fluoro alkyl group content silane compound which the basis of an acid catalyst was made to hydrolyze on a base material front face, and relates to the base material in which the water-repellent coat which consists of a monomolecular layer was formed.
[0012] Moreover, this invention fixes the monomer of the hydrolyzate of the fluoro alkyl group content silane compound which the basis of an acid catalyst was made to hydrolyze on a base material front face. Are a solution for forming the water-repellent coat which consists of a monomolecular layer, and the solution containing this monomer makes concentration of a fluoro alkyl group content silane compound 0.1 - 15 % of the weight. And it is related with the solution for water-repellent coat formation characterized by being generated using the solution which used alcohol equal to the class of alkoxy group in this alkoxy group content silane compound as the diluent solvent, and made aqueous acids the catalyst.
[0013] Moreover, as for said fluoro alkyl group content silane compound, it is desirable that it is the fluoro alkyl alkoxysilane compound expressed with a general formula [1].
CF3(CF2)m(CH2)nSiR1x(OR2)3-x [1]
(Each integer of m=0-15, n=0-2, x=0-2, however m+n=0-17, R1, R2=CH3, C2H5, C3H5, and C4H7 are expressed among a formula)
Furthermore, as for the hydrolyzate of a fluoro alkyl group content silane compound, it is desirable to consist of 99.5% of the weight or more of a monomer.
[0014] Furthermore, this invention relates to the formation approach of the water-repellent coat which consists of a process which applies the above-mentioned solution for water-repellent coat formation to a base material front face, and a hardening process which fixes the fluoro alkyl group subsequently to this solution contained on this base material front face, and forms the water-repellent coat of a monomolecular layer.
[0015]
[Embodiment of the Invention] The solution for water-repellent coat formation which forms the high endurance water repellence coat of this invention can be obtained by carrying out predetermined time churning and making a hydrolysis reaction end, after carrying out specified quantity mixing of the water repellent which consists of a fluoro alkyl group content silane compound, the solvent for dilution, and the aqueous acids as a catalyst.
[0016] As the above-mentioned start raw material, it is a fluoro alkyl alkoxysilane system compound as water repellent. As the compound for example, -- CF -- three -- CH -- two -- CH -- two -- Si -- (-- OR --) -- three -- CF -- three (CF2) -- five -- CH -- two -- CH -- two -- Si -- (-- OR --) -- three -- CF -- three (CF2) -- five -- CH -- two -- CH -- two -- SiR -- (-- OR --) -- two -- CF -- three (CF2) -- seven -- CH -- two -- CH -- two -- Si -- (-- OR --) -- three -- CF -- three (CF2) -- seven -- CH -- two -- CH -- two -- SiR -- (-- OR --) -- two -- etc. etc. -- It can use. In addition, R in the above-mentioned chemical formula shows CH3, C2H5, and C3H7.
[0017] Moreover, as a diluent solvent, five or less lower alcohol solvent has desirable carbon numbers other than isopropyl alcohol (it abbreviates to "i-PA" hereafter), such as a methanol and ethanol, using alcohol equal to the class of alkoxy group in the alkoxy group content silane compound of the above-mentioned water repellent.
[0018] Moreover, 0.01Ns or more of organic acids, such as inorganic acids, such as a nitric acid of about [0.1N-3N] concentration, a hydrochloric acid, and a sulfuric acid, or an acetic acid, and a citric acid, can be preferably used for the aqueous acids as a catalyst. In addition, a water-repellent:dilution solvent: At a weight rate, although the range of aqueous acids of 1:12.5-40:0.09-1.0 is desirable, they are not limited to these range. Furthermore, as for the hydrolyzate of the fluoro alkyl group content silane compound in the solution for water-

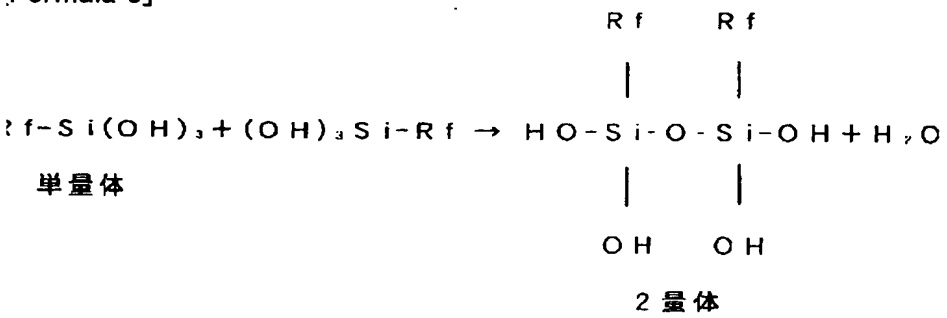
repellent coat formation, it is desirable to consist of 99.5% of the weight or more of a monomer.
[0019] Next, hydrolysis and the polycondensation reaction of a fluoro alkyl group content silane compound are explained.
(1) As shown in a degree type, under an acid catalyst, the hydrolysis reaction fluoro (alkyl Rf) radical content silane compound (a degree type is the example of an alkoxysilane compound) reacts with water, and is hydrolyzed comparatively easily. In addition, about a hydrolysis reaction, although the time amount for about 120 minutes is preferably required about about 90 minutes to obtain the conclusion of a hydrolysis reaction (stirring), it is not limited to this.
[0020]
[Formula 1]



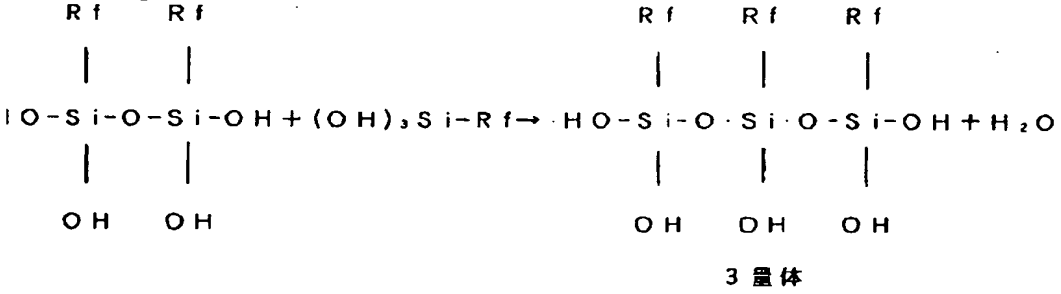
[0021] a dehydration condensation reaction [like the silanol group on the front face of glass (-SiOH), and a degree type] whose hydrolyzate (monomer) of the fluoro alkyl group content silane compound (FAS) obtained by the upper type is -- carrying out -- a glass substrate top -- immobilization -- or it changes a high polymer (probably child).
[0022] ** A reaction with glass [0023]
[Formula 2]



[0024] (2) Polymerization degree increases by the reaction reaction FAS [polycondensation reaction **FAS]. Generally, polymerization degree increases by the hydrolyzed FAS ** FAS polycondensation reaction. Then, this invention controls this reaction by limiting the content of the fluoro alkyl group content silane compound in the solution for water-repellent coat formation, and the class of dilution solvent.
[0025] - Dimerization [0026]
[Formula 3]



[0027] - 3 quantification [0028]
[Formula 4]



[0029] In addition, the concentration of the FAS compound in the solution for water-repellent coat formation has 0.1 - 15 desirable % of the weight, and a wear-resistant good monomolecular layer is not obtained except this range. This is because dimerization by the FAS reaction of [-izing 2] and further 3 quantification are promoted

by FAS high concentration-ization. It is 1.0 - 8.0 % of the weight more preferably.
[0030] If it is ingredients, such as glass with which active hydrogen, such as a hydroxyl group (- OH), is contained on the front face, plastics, and ceramics, as a base material, when anything can be used and active hydrogen is not included on a front face, what introduced the hydroxyl group into the base material front face by plasma treatment or corona treatment can be applied.
[0031] As a glass base material which is one of the typical base materials Sheet glass with the transparency of minerals, such as glass manufactured by the float glass or the roll-out method usually used for the structural windowpane, the windowpane for automobiles, etc., is desirable. It is not what is limited to combination with colorlessness or coloring and its class or a color tone, and other functional film, especially a configuration, etc. Furthermore as bending sheet glass, of course, it is various tempered glass and on-the-strength rise glass, and while being able to use it with a plate or the veneer, it can be used also as multiple glass or laminated glass. Moreover, a coat may form membranes to both sides of a glass substrate. Furthermore, the conditions which apply the solution for water-repellent coat formation on the front face of a glass substrate are not limited to these, although below about 50%RH extent usually has desirable ambient atmosphere humidity.
[0032] Furthermore, although it is clearly different in the top side and bottom side of this glass in the case of a float glass, and it is desirable to carry out a coat to the top side which is a fire-polishing side of a float glass and it is desirable about the surface state of a glass substrate to cover to the fire-polishing side which does not touch a conveyance roll etc. also about the glass similarly manufactured by the roll-out method, it can cover also with a bottom side or a non-fire-polishing side depending on the case. If surface treatment is carried out by carrying out polishing processing beforehand and carrying out acid treatment of the front face of the glass substrate which applies the solution for water-repellent coat formation, the reinforcement of a coat etc. increases, and although it is desirable, as the approach is the following, it will be performed.
[0033] The Flo-toga lath top side with little mixing of tin to the polishing processing for the surface treatment of a glass substrate, Roll-out glass sides or these bending, a tempered glass side, etc. Detailed fine particles which use inorganic metallic oxides, such as cerium oxide (Seria), an aluminum oxide (alumina), or/and oxidation silicon, as a principal component (mean particle diameter about 5 micrometers or less) It is changing suitably the class of fine particles used in respect of polishing of a brush, sponge, or cloth by wet or dry type, the quality of the material of the particle size and a polishing side, contact pressure with a glass substrate, etc. using the surface abrasives which is about 1 micrometer or less preferably. It is desirable to polish controlling the surface crack condition and polishing condition of said glass substrate side.
[0034] This glass side that carried out polish processing Subsequently, an inorganic acid or acetic acids, such as a hydrochloric acid, a sulfuric acid, and a nitric acid, Organic acids, such as a formic acid or oxalic acid, by for example, the thing which the temperature of acid-treatment liquid does for acid treatment under 5 degrees C - 70 degrees C or less and the conditions not more than processing-time 10 second -10 minute, using the acid-treatment liquid which becomes in the water solution which carried out addition adjustment so that it might be set to 4 or less concentration of pH The extract of the sodium ion on the front face of glass and cutting of siloxane association which carried out polishing processing shall generate a silanol group efficiently, and this silanol group shall contribute to immobilization of a water-repellent fluoro alkyl group in a water-repellent finish of a back process. In addition, although carried out by being immersed into an acid solution, to others, especially f acid treatment is approaches by which dip coating, an EQC, or the approximated acid-treatment effectiveness s acquired, such as a spray method and a Floe process, it is not limited, and can be adopted.
[0035] Furthermore, as a film attachment method to a glass substrate, a known spreading means, the various applying methods these people made [the methods etc.] the application proposal further, such as hand coating the rubbing method), the nozzle flow coat method, a dipping method, a spray method, the liver skorts method, the flexo method, print processes, the flow coat method or spin coat methods, and those concomitant use, can adopt suitably. Moreover, it is desirable to perform curing for 1 minute thru/or for 60 minutes, and to form membranes as heat treatment conditions after membrane formation, for example below 80 degrees C or more 150 degrees C.
0036]
Function] The efficiency of the reactivity on a water repellent component and the front face of a base material s increased, and this invention becomes possible [forming the monomolecular layer by which densification of he fluoro alkyl group was carried out to the base material front face] by considering as the solution for water-epellent coat formation carried out as [form / as a principal component / by controlling hydrolysis and the olycondensation reaction of the solution for water-repellent coat formation / only a monomer], covering with he bottom of the controlled covering environment on a base material front face, and forming a thin film. it has he abrasion resistance which boiled the obtained water-repellent film markedly and was excellent, and it is a igh degree of hardness and high adhesion, and has endurance, and the water-repellent engine performance /hich was excellent in the long run, for example, a contact angle, can maintain about 90 degrees or more.
0037]

[Example] Hereafter, an example explains this invention concretely. However, this invention is not limited to the starting example.
[0038] Preparation of the solution for example 1 water-repellence coat formation was performed by [as being the following]. As a raw material of the solution presentation for water-repellent coat formation for forming a water-repellent coat Fluoro alkyl triisopropoxy silane [CF3(CF2)7CH2CH2Si3 (it abbreviates to "FAS-P" hereafter) (OC3H7); Toshiba Silicone XC95-A9715], The isopropyl alcohol which is alcohol equal to the class of alkoxy group of the water repellent used for a diluent solvent [(it abbreviates to "i-PA" hereafter) the product made from; KISHIDA chemistry], Using 0.1N-nitric acid [the product made from KISHIDA chemistry] which is an acid catalyst, the blending ratio of coal was made into FAS-P:i-PA:0.1 N-HNO 3= 1:12.5:0.3 (unit: g), it stirred at the room temperature for about 2 hours, the hydrolysis reaction was performed, and the solution for water-repellent coat formation was prepared.
[0039] As a result of measuring the abundance of the monomer in this solution which can be set FAS, as shown in Table 1, the monomer was [the trimer of the dimer] 0 % of the weight 0.5% of the weight 99.5% of the weight. In addition, measurement of polymerization degree was performed by the following approaches.
[Polymerization-degree measurement]
Measuring method : gel par MYUESHON chromatography method (following it abbreviates to "GPC")
Measuring equipment : high-speed-gel-permeation-chromatography equipment HLC-8020 (TOSOH make)
column :TSKgelG4000 H-HR and G3000 H-HR four columns (30cm each) of G2000 H-HR and G2000 H-HR (all are TOSOH make) -- a serial -- **** it is -- thing (the temperature of a column is held at 40 degrees C)
Detector : differential refractometer (the temperature of a detector is held at 38 degrees C)
Eluate : tetrahydrofuran (a flow rate is a part for 1l./)
Injection rate of the solution for water-repellent coat formation : The solution sample for water-repellent coat formation for GPC measurement which is 50microl In order to inactivate a silanol group and to enlarge a refractive-index difference with an eluate more further After carrying out the trimethylsilylation of the FAS hydrolyzate and the polycondensation object in this solution using the trimethylchlorosilane (CH3) (3 SiCl:TMCS) which is one of the TMS(trimethylsilyl)-ized agents, the sample (solution for water-repellent coat formation) was filtered with the filter of 0.5 micrometers of apertures. the reaction condition for trimethylsilylation -- a 5g sample (solution for water-repellent coat formation) -- receiving -- 0.57g TMCS -- in addition, 1h was agitated at the room temperature. From each peak in the obtained GPC chart, the holding time of an FAS monomer (Monomer), a dimer (Dimer), and a trimer (Trimer) has been identified 32.5, 30.8, and 29.9 minutes in the solution for dehydration water repellence coat formation.
[0040] Moreover, it asked for the abundance ratio of each polymer by the ratio of a peak area. (However, it was assumed that the refractive index of the TMS compound of a monomer, a dimer, and a trimer did not change) .
[0041] Then, formation of a water-repellent coat on a base material front face was performed by [as being the following]. Using polishing liquid and a brush polisher, after polishing, the abrasives was fully removed and the front face of the float glass substrate of 200mmx300mmx3.5mm size was immersed for 1 minute into 35-degree C 0.1-N sulfuric-acid water solution. Then, after rinsing and drying with the commercial glass soaping machine, dropping the solution for 2ml [per glass substrate //sheet] water repellence coat formation under the environment which maintained temperature and humidity at RH 23 degrees C and 45% and a cheesecloth's (trade name BEMCOT's) extending enough all over glass, grade air-drying was carried out for 5 minutes. Then, the glass substrate was thrown in in the muffle furnace, after performing heat treatment (it is hereafter called curing) in which the temperature of this glass substrate amounts to 140 degrees C in 5 minutes, the surplus water repellent which becomes cloudy and remains in drawing and a glass substrate front face from the inside of a furnace had been wiped with the cheesecloth in which i-PA was included, and the transparent water-repellent glass substrate was obtained. in addition, the above-mentioned polishing liquid -- MIREKU (A+B) (product made from Mitsui Mining & Smelting industry):water =1:100 (% of the weight) -- suspension was used.
[0042] The initial-contact angle of the obtained glass with a water-repellent coat showed 108 degrees and high water repellence. In addition, the following approach estimated the water-repellent sex test.
[0043]
[Water-repellent sex test]
Measuring equipment : CA-X200 mold made from consonance interface science Measurement environment : inside of atmospheric air (about 25 degrees C)
Water : Waterdrop of pure water (2microl) Evaluation : The above-mentioned waterdrop is dropped on a glass side, and they are this glass and water. Include angle which a drop makes (degree) (that is, it is called a contact angle)
t measured.
0044] As compared with example 2 example 1, the concentration of water repellent is lowered and the blending ratio of coal of a raw material is made into FAS-P:i-PA:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 1, and were performed.

[0045] a result -- Table 1 -- being shown -- as -- a monomer -- in abundance, the dimer was able to obtain the solution for water-repellent coat formation with which a trimer is 0 and consists only of a monomer mostly 0.1% of the weight 99.9% of the weight. In addition, as a result of measuring the traverse-proof nature of the obtained glass with a water-repellent coat, it was stabilized with 93-105 degrees, the high value was acquired, and it was good. In addition, the following approach estimated traverse-proof nature.
[0046]
[Abrasion resistant test]
Testing machine : traverse type sliding testing machine (manufacture machine of our company)
Sample size : Abbreviation 200mmx300mm Load to a friction cloth : It is 0.1kg/cm2 (JIS L 3102-1206) to a canvas cloth.
Stroke : 100mm both-way sliding (the count of sliding is a count of a round trip)
Sliding rate : A part for 30 round-trip/ Evaluation : Measurement of contact angle [after 3500 counts of sliding] theta (degree).
[0047] As compared with example 3 example 1, the concentration of water repellent is lowered and the blending ratio of coal of a raw material is made into FAS-P:i-PA:0.1 N-HNO 3= 1:50:0.3 (unit: g). In addition, other conditions were the same as the example 1, and were performed.
[0048] a result -- Table 1 -- being shown -- as -- a monomer -- in abundance, the dimer was able to obtain the solution for water-repellent coat formation with which a trimer is 0 and consists only of a monomer mostly 0.1% of the weight 99.9% of the weight.
[0049] As compared with example 4 example 1, the concentration of water repellent is lowered and the blending ratio of coal of a raw material is made into FAS-P:i-PA:0.1 N-HNO 3= 1:75:0.3 (unit: g). In addition, other conditions were the same as the example 1, and were performed.
[0050] a result -- Table 1 -- being shown -- as -- a monomer -- in abundance, the dimer was able to obtain the solution for water-repellent coat formation with which a trimer is 0 and consists only of a monomer mostly 0.1% of the weight 99.9% of the weight.
[0051] It compares with example 5 example 1. As water repellent Fluoro alkyl trimethoxysilane [CF3(CF2) 7CH2CH2Si (OCH3)3 (it abbreviates to "FAS-M" hereafter), and KBM-7803made from Shin-etsu chemistry], The methanol which is alcohol equal to the class of alkoxy group of the water repellent used for a diluent solvent [(it abbreviates to "MeOH" hereafter) the product made from; KISHIDA chemistry], Using 0.1N-nitric acid [the product made from KISHIDA chemistry] which is an acid catalyst, the blending ratio of coal was made into FAS-M:MeOH:0.1 N-HNO 3= 1:25:0.3 (unit: g), it stirred at the room temperature for about 2 hours, and the hydrolysis reaction was performed. In addition, other conditions were the same as the example 1, and were performed.
[0052] a result -- Table 1 -- being shown -- as -- a monomer -- in abundance, the dimer was able to obtain the solution for water-repellent coat formation with which a trimer is 0 and consists only of a monomer mostly 0.5% of the weight 99.5% of the weight.
[0053] As compared with example of comparison 1 example 1, the concentration of water repellent is raised and the blending ratio of coal of a raw material is made into FAS-P:i-PA:0.1 N-HNO 3= 1:5:0.3 (unit: g). In addition, other conditions were the same as the example 1, and were performed.
[0054] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.3 % of the weight and the trimer of 98.7 % of the weight and a dimer] 0, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0055] The GPC chart which measured the solution for water-repellent coat formation of the above-mentioned examples 1-4 and the example 1 of a comparison after trimethylsilylation to drawing 1 is shown. In the examples 1-4 whose concentration of the water repellent in a result and the solution for water-repellent coat formation is 15 or less % of the weight, as for the example 1 of a comparison this whose concentration is 15 % of the weight or more, the peak of a dimer has appeared clearly to the peak of a dimer having hardly appeared. In addition, the curve respectively corresponding to [** / in drawing / ** / an example 1 and / corresponding to / ** / an example 4 and / an example 3 in an example 2 and **] the example 1 of a comparison in ** is shown.
[0056] As compared with example of comparison 2 example 2, a diluent solvent is used as a methanol and the blending ratio of coal of a raw material is made into FAS-P:MeOH:0.1 N-HNO 3= 1:25:0.3 (unit: g).
[0057] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.0 % of the weight and the trimer of 99.0 % of the weight and a dimer] 0, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0058] As compared with example of comparison 3 example 2, a diluent solvent is made into ethanol [(it abbreviates to "EtOH" hereafter) the product made from; KISHIDA chemistry], and the blending ratio of coal of a raw material is made into FAS-P:EtOH:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 2, and were performed.
[0059] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.0 % of the weight and the trimer of 99.0 % of the weight and a dimer] 0, and 99.5% of the weight or more of target monomer concentration

was not obtained.
[0060] As compared with example of comparison 4 example 2, a diluent solvent is made into n-butanol [(it abbreviates to "BuOH" hereafter) the product made from; KISHIDA chemistry], and the blending ratio of coal of a raw material is made into FAS-P:BuOH:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 2, and were performed.
[0061] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.0 % of the weight and the trimer of 99.0 % of the weight and a dimer] 0, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0062] The GPC chart which measured the solution for water-repellent coat formation of an example 2 and the examples 2-4 of a comparison after trimethylsilylation to drawing 2 is shown. a result -- the same solvent (i-PA) as FAS-P -- having used -- an example -- two -- **** -- a dimer -- although most peaks have not appeared, in the examples 2-4 of a comparison using other solvents, the peak of a dimer has appeared clearly. In addition, the curve respectively corresponding to [** / in drawing / corresponding to / ** / the example 3 of a comparison and / the example 2 of a comparison in an example 2 and **] the example 4 of a comparison in ** is shown.
[0063] As compared with example of comparison 5 example 5, a diluent solvent is made into ethanol and the blending ratio of coal of a raw material is made into FAS-M:EtOH:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 5, and were performed.
[0064] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.4 % of the weight and the trimer of 98.6 % of the weight and a dimer] 0, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0065] As compared with example of comparison 6 example 5, a diluent solvent is made into isopropyl alcohol and the blending ratio of coal of a raw material is made into FAS-M:i-PA:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 5, and were performed.
[0066] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.4 % of the weight and the trimer of 98.4 % of the weight and a dimer] 0.2, and 99.5% of the weight or more of target monomer concentration was not obtained. In addition, as a result of measuring traverse-proof nature, 50-100 degrees and an unstable value were shown, and it was not desirable.
[0067] As compared with example of comparison 7 example 5, a diluent solvent is made into a butanol and the blending ratio of coal of a raw material is made into FAS-M:BuOH:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 5, and were performed.
[0068] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [1.3 % of the weight and the trimer of 98.5 % of the weight and a dimer] 0.2, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0069] As compared with example of comparison 8 example 5, a diluent solvent is used as an acetone and the blending ratio of coal of a raw material is made into FAS-M:acetone:0.1 N-HNO 3= 1:25:0.3 (unit: g). In addition, other conditions were the same as the example 5, and were performed.
[0070] a result -- Table 1 -- being shown -- as -- a monomer -- abundance is [9.1 % of the weight and the trimer of 90.4 % of the weight and a dimer] 0.5, and 99.5% of the weight or more of target monomer concentration was not obtained.
[0071] As compared with example of comparison 9 example 5, the blending ratio of coal of a raw material which does not add an acid catalyst (0.1-N nitric acid) is made into FAS-M:MeOH:0.1 N-HNO 3= 1:25:0 (unit: g). In addition, other conditions were the same as the example 5, and were performed.
[0072] a result -- Table 1 -- being shown -- as -- a monomer -- although the dimer and the trimer of abundance were 0 99.9% of the weight or more, the initial-contact angle was as low as 90 degrees, and was suggested in the solution for water-repellent coat formation, saying that in which the hydrolysis reaction has not occurred at all. In addition, as a result of measuring traverse-proof nature, it was 60 degrees or less in value, and was not desirable.
[0073]
Table 1]

サンプルNo.	撥水剤の種類	溶媒の種類	酸触媒の種類	撥水液中の撥水剤濃度(wt%)	撥水液中のFAS重合体含有割合(wt%)		
					3量体	2量体	単量体
実施例1	FAS-P	i-PA	HNO3	7.2	0	0.5	99.5
実施例2	FAS-P	i-PA	HNO3	3.8	0	0.1	99.9
実施例3	FAS-P	i-PA	HNO3	1.9	0	0.1	99.9
実施例4	FAS-P	i-PA	HNO3	1.3	0	0.1	99.9
実施例5	FAS-M	MeOH	HNO3	3.8	0	0.5	99.5
比較例1	FAS-P	i-PA	HNO3	15.9	0	1.3	98.7
比較例2	FAS-P	MeOH	HNO3	3.8	0	1.0	99.0
比較例3	FAS-P	EtOH	HNO3	3.8	0	1.0	99.0
比較例4	FAS-P	BuOH	HNO3	3.8	0	1.0	99.0
比較例5	FAS-M	EtOH	HNO3	3.8	0	1.4	98.6
比較例6	FAS-M	i-PA	HNO3	3.8	0.2	1.4	98.4
比較例7	FAS-M	BuOH	HNO3	3.8	0.2	1.3	98.5
比較例8	FAS-M	アセトン	HNO3	3.8	0.5	9.1	90.4
比較例9	FAS-M	MeOH	なし	3.8	0	0	＞99.9

[0074]

[Effect of the Invention] As mentioned above, according to this invention, the extremely excellent abrasion resistance (traverse-proof nature) is shown. Since stability and the water-repellent engine performance which was certainly excellent are maintained under mass production, water-repellent base materials, such as glass with high endurance, are obtained efficiently simple, homogenization of quality is improved and an optical property is not spoiled The object for construction can offer the useful solution for water-repellent coat formation with high utility value widely employable as various kinds of goods, such as mirrors the aperture material for automobiles, the aperture material of a vessel or the aircraft, the object for bathrooms, for automobiles, etc., and industrial glass, from the first.

[Translation done.]

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号

特開平11－322368

(43)公開日　平成11年(1999)11月24日

(51)Int.Cl.[6]	識別記号	ＦＩ	
Ｃ０３Ｃ　17/30		Ｃ０３Ｃ　17/30	Ｂ
Ｃ０９Ｋ　3/18	１０２	Ｃ０９Ｋ　3/18	１０２

審査請求　未請求　請求項の数5　ＯＬ　（全９頁）

(21)出願番号　特願平10－132876

(22)出願日　平成10年(1998)５月15日

(71)出願人　000002200
セントラル硝子株式会社
山口県宇部市大字沖宇部5253番地

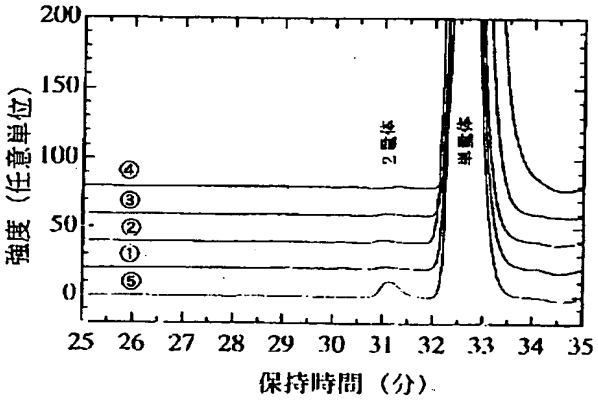
(72)発明者　赤松　佳則
三重県松阪市大口町1510　セントラル硝子株式会社硝子研究所内

(72)発明者　濱口　滋生
三重県松阪市大口町1510　セントラル硝子株式会社硝子研究所内

(74)代理人　弁理士　西　義之

(54)【発明の名称】　撥水性被膜形成用溶液

(57)【要約】
【課題】高硬度かつ高密着性であって、耐久性や耐摩耗性を併せ持ち、より長期的に優れた撥水性能を維持する撥水性被膜の形成方法および該被膜を形成した基材を提供する。
【解決手段】酸触媒のもとに加水分解させたフルオロアルキル基含有シラン化合物の加水分解物の単量体を基材表面に固定化し、単分子層からなる撥水性被膜を形成すること。



【特許請求の範囲】

【請求項１】酸触媒のもとに加水分解させたフルオロアルキル基含有シラン化合物の加水分解物の単量体を基材表面に固定化し、単分子層からなる撥水性被膜を形成したことを特徴とする基材。

【請求項２】酸触媒のもとに加水分解させたフルオロアルキル基含有シラン化合物の加水分解物の単量体を基材表面に固定化し、単分子層からなる撥水性被膜を形成するための溶液であって、該単量体を含む溶液はフルオロアルキル基含有シラン化合物の濃度を０．１～１５重量％とし、且つ該アルコキシ基含有シラン化合物中のアルコキシ基の種類と等しいアルコールを希釈溶媒とし、酸性水溶液を触媒とした溶液を用いて生成されたものであることを特徴とする撥水性被膜形成用溶液。

【請求項３】前記フルオロアルキル基含有シラン化合物は、一般式［１］で表されるフルオロアルキルアルコキシシラン化合物であることを特徴とする請求項２記載の撥水性被膜形成用溶液。

$$CF_3(CF_2)_m(CH_2)_nSiR^1_x(OR^2)_{3-x} \qquad [1]$$

（式中、ｍ＝０～１５、ｎ＝０～２、ｘ＝０～２、ただし、ｍ＋ｎ＝０～１７の各整数、R^1、R^2＝CH_3、C_2H_5、C_3H_5およびC_4H_7を表す）

【請求項４】フルオロアルキル基含有シラン化合物の加水分解物は９９．５重量％以上の単量体からなることを特徴とする請求項２乃至３記載の撥水性被膜形成用溶液。

【請求項５】請求項２乃至４記載の撥水性被膜形成用溶液を基材表面に塗布する工程と、次いで該撥水性被膜形成用溶液に含まれるフルオロアルキル基を該基材表面に固定化し単分子層の撥水性被膜を形成する硬化工程とからなることを特徴とする撥水性被膜の形成方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、建築用、自動車用、船舶用或いは航空機用等の各種窓材、浴室用或いは自動車用等のミラー、さらにはその他産業用など種々の分野の各種透明物品等に利用できるガラス基板等の基材表面に撥水性被膜を形成するための溶液および撥水性被膜の形成方法ならびに該被膜を形成した基材に関するものである。

【０００２】

【従来の技術】最近、より優れた耐久性と撥水性を併せ持ち、優れた撥水性能をより長く持続する透明な撥水性被膜が望まれてきている。これらのニーズに答えるためには、例えば高い耐摩耗性（耐トラバース性）を有する撥水性薄膜を備える撥水性基材とする必要がある。

【０００３】そこで、本出願人が既に出願した特願平７－２９４１０６号（特開平９－１３２４３３号公報）等に記載している発明は、ガラス表面に高硬度で高機械的強度、かつ耐久性に優れた高い比表面積で制御した特異で微細な凹凸形状表層表面を有するベース膜を形成し、該ベース膜を被覆する撥水膜を形成することで、該撥水膜の付着効率と密着性を高め、さらに耐光性能を向上するようにしたものである。

【０００４】また、本出願人が既に出願した特願平８－１３１５９５号（特開平９－３０９７４６号公報）等に記載している発明は、ガラス基板の表面に撥水膜を形成する際に、ガラス基板の温度が９０～２００℃程度にある状態でガラス基板表面（場合によっては方向性をもつ筋状の疵をつけた微細な凹凸状ガラス基板表面）に撥水膜層を形成することとし、耐候性、耐摩耗性、耐擦傷性ならびに耐久性に格段に優れた撥水性能を発揮するようにしたものである。

【０００５】また、特許第２５００１７８号には、基材表面の撥水撥油処理方法として、フッ化炭素基とクロル基を複数個含むシラン系化合物を用いてガラス基板などの基材表面に化学吸着単分子層を形成する方法が示されており、フルオロアルキル基含有クロロシラン化合物を非水系の溶媒に溶解した溶液に基板を浸漬する工程と、基材を取り出した後、水分を全く含まないかまたは実質的に含まない雰囲気中で乾燥する工程が示されており、基材表面に形成された単分子層は優れた耐摩耗性を発揮することが示されている。

【０００６】

【発明が解決しようとする課題】上述した例えば、特願平７－２９４１０６号に記載の撥水性のガラスは、前述したニーズに充分に答えうるものであるものの、特異なベース膜と撥水膜の２層構造の膜構成と複雑であり、単純で簡便な下地層を必要としない層であって、より高性能を有する撥水性ガラスも望まれているところである。

【０００７】また、特願平８－１３１５９５号等に記載の撥水性ガラスは、製造時における作業性、特にガラス基板温度を９０～２００℃に高めた状態に管理する必要があるため、その取り扱いが充分に簡便で高効率であるとは言い難い場合がある。

【０００８】また、特許第２５００１７８号に記載のガラス表面の撥水撥油剤に開示されている方法では、クロロシラン系化合物が極めて水に対して反応性が高いため、多くの工程を水分のない極めて乾燥した環境下で行う必要があるなど、取り扱いが極めて厄介である。

【０００９】すなわち、従来の単分子層を形成させるものや、耐久性能を向上させるために下地膜を形成させるものは、複雑な管理条件と工程を要しコスト高になっており、一方下地膜のないものでは、一般的に撥水剤成分とガラス表面との反応性が不十分であったり、フルオロアルキル基含有クロロシランのような反応性の高い化合物を取り扱う必要があった。

【００１０】

【課題を解決するための手段】本発明は、従来のかかる

課題に鑑みてなしたものであって、撥水性被膜形成用溶液中のフルオロアルキル基含有シラン化合物の含有量および希釈溶媒の種類を限定することにより、得られた撥水性被膜形成用溶液はフルオロアルキル基含有シラン化合物の加水分解物の単量体のみからなり、この溶液を塗布して得られた撥水性被膜は単分子層が形成され、該膜は高硬度かつ高密着性であって耐久性や耐摩耗性とを併せ持ち、より長期的に優れた撥水性能を有することを見出したものであり、下地層が不要で且つ常温で成膜できるとともに、反応性の高い化合物を取り扱う必要もない、非常に操作の容易な撥水性被膜の形成方法および該被膜を形成した基材である。

【００１１】すなわち本発明は、酸触媒のもとに加水分解させたフルオロアルキル基含有シラン化合物の加水分解物の単量体を基材表面に固定化し、単分子層からなる撥水性被膜を形成した基材に関する。

【００１２】また本発明は、酸触媒のもとに加水分解させたフルオロアルキル基含有シラン化合物の加水分解物の単量体を基材表面に固定化し、単分子層からなる撥水性被膜を形成するための溶液であって、該単量体を含む溶液はフルオロアルキル基含有シラン化合物の濃度を０．１～１５重量％とし、且つ該アルコキシ基含有シラン化合物中のアルコキシ基の種類と等しいアルコールを希釈溶媒とし、酸性水溶液を触媒とした溶液を用いて生成されたものであることを特徴とする撥水性被膜形成用溶液に関する。

【００１３】また、前記フルオロアルキル基含有シラン化合物は、一般式［１］で表されるフルオロアルキルアルコキシシラン化合物であることが好ましい。

$$CF_3(CF_2)_m(CH_2)_nSiR^1_x(OR^2)_{3-x} \qquad [1]$$

（式中、m＝0～１５、n＝0～2、x＝0～2、ただし、m＋n＝0～１７の各整数、R^1、R^2＝CH_3、C_2H_5、C_3H_5およびC_4H_7を表す）

さらに、フルオロアルキル基含有シラン化合物の加水分解物は９９．５重量％以上の単量体からなることが好ましい。

【００１４】さらに本発明は、上記撥水性被膜形成用溶液を基材表面に塗布する工程と、次いで該溶液に含まれるフルオロアルキル基を該基材表面に固定化し単分子層の撥水性被膜を形成する硬化工程とからなる撥水性被膜の形成方法に関する。

【００１５】

【発明の実施の形態】本発明の高耐久性撥水性被膜を形成する撥水性被膜形成用溶液は、フルオロアルキル基含有シラン化合物からなる撥水剤と、希釈用の溶媒と、触媒としての酸性水溶液を所定量混合したのち、所定時間撹拌して加水分解反応を終結させることにより得ることができる。

【００１６】上記の出発原料としては、撥水剤としてフルオロアルキルアルコキシシラン系化合物であり、その化合物としては、例えば$CF_3CH_2CH_2Si(OR)_3$、$CF_3(CF_2)_5CH_2CH_2Si(OR)_3$、$CF_3(CF_2)_5CH_2CH_2SiR(OR)_2$、$CF_3(CF_2)_7CH_2CH_2Si(OR)_3$、$CF_3(CF_2)_7CH_2CH_2SiR(OR)_2$、等を用いることが出来る。なお、上記化学式におけるRはCH_3、C_2H_5、C_3H_7を示す。

【００１７】また、希釈溶媒としては、上記撥水剤のアルコキシシラン化合物中のアルコキシ基の種類と等しいアルコールを用い、イソプロピルアルコール（以下、「ｉ－ＰＡ」と略す）の他に、メタノール、エタノールなど炭素数が５以下の低級アルコール溶媒が好ましい。

【００１８】また、触媒としての酸性水溶液は、０．０１Ｎ以上、好ましくは０．１Ｎ～１３Ｎ程度の濃度の硝酸、塩酸、硫酸などの無機酸あるいは、酢酸、クエン酸などの有機酸を使用することができる。なお、撥水剤：希釈溶剤：酸性水溶液は、重量割合で１：１２．５～４０：０．０９～１．０の範囲が好ましいが、これらの範囲に限定されるものではない。さらに、撥水性被膜形成用溶液中のフルオロアルキル基含有シラン化合物の加水分解物は９９．５重量％以上の単量体からなることが好ましい。

【００１９】次に、フルオロアルキル基含有シラン化合物の加水分解および重縮合反応について説明する。

（１）加水分解反応

フルオロアルキル（Ｒｆ）基含有シラン化合物（次式はアルコキシシラン化合物の例）は次式に示すように、酸触媒下で水と反応して比較的容易に加水分解される。なお、加水分解反応については、加水分解反応（撹拌）の終結を得るには約９０分程度、好ましくは約１２０分程度の時間が必要であるが、これに限定されるものではない。

【００２０】

【化１】

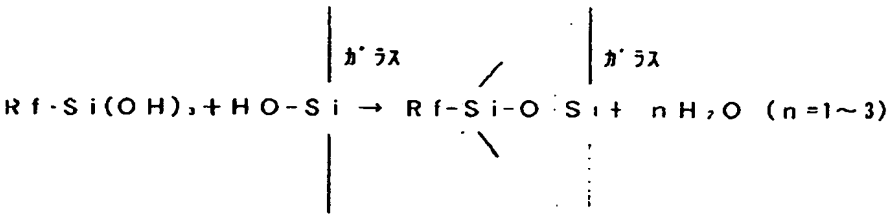
$$Rf-Si(OCH_3)_3 + 3H_2O \xrightarrow{\text{酸（硝酸）触媒}} Rf-Si(OH)_3 + 3MeOH$$

【００２１】上式により得られたフルオロアルキル基含有シラン化合物（ＦＡＳ）の加水分解物（単量体）は、ガラス表面のシラノール基（－ＳｉＯＨ）と次式のような脱水縮合反応をし、ガラス基板上へ固定化または高重合体（多分子）化する。

【００２２】①ガラスとの反応

【００２３】

【化２】



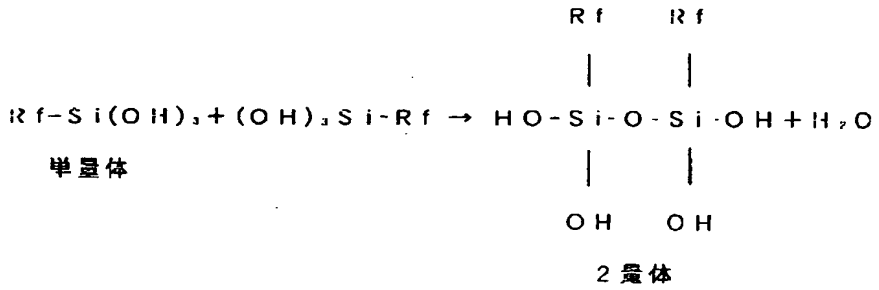
ｶﾞﾗｽ基板へのＲｆ基の固定化

【００２４】（２）重縮合反応
❷ＦＡＳ同士の反応
ＦＡＳ同士の反応により重合度が増加する。一般的には、加水分解したＦＡＳはＦＡＳ同士の重縮合反応により重合度が増加する。そこで、本発明は撥水性被膜形成用溶液中のフルオロアルキル基含有シラン化合物の含有量および希釈溶剤の種類を限定することにより、この反応を抑制するものである。

【００２５】・２量化

【００２６】

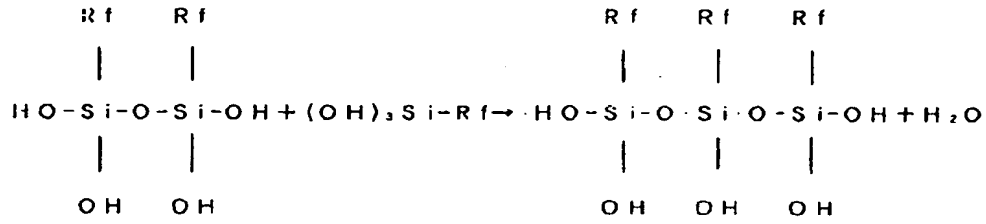
【化３】



【００２７】・３量化

【００２８】

【化４】



【００２９】なお、撥水性被膜形成用溶液中のＦＡＳ化合物の濃度は０．１～１５重量％が好ましく、この範囲以外では耐摩耗性の良好な単分子層が得られない。これは、ＦＡＳの高濃度化により〔化２〕のＦＡＳ同士の反応による２量化、さらには３量化が促進されるためである。より好ましくは１．０～８．０重量％である。

【００３０】基材としては、表面に水酸基（－ＯＨ）等の活性水素が含まれているガラス、プラスチック、セラミックス等の材料であれば何でも用いることが出来、また、表面に活性水素を含まない場合に、プラズマ処理あるいはコロナ処理等で基材表面に水酸基を導入したものでも適用できる。

【００３１】代表的基材の一つであるガラス基材としては、建築用窓ガラスや自動車用窓ガラス等に通常使用されているフロートガラスあるいはロールアウト法で製造されたガラス等無機質の透明性がある板ガラスが好ましく、無色または着色、ならびにその種類あるいは色調、他の機能性膜との組み合わせ、形状等に特に限定されるものではなく、さらに曲げ板ガラスとしてはもちろん各種強化ガラスや強度アップガラスであり、平板や単板で使用できるとともに、複層ガラスあるいは合せガラスとしても使用できる。また、被膜はガラス基板の両面に成膜しても構わない。さらに、撥水性被膜形成用溶液をガラス基板の表面上に塗布する条件は、通常雰囲気湿度が約５０％ＲＨ以下程度が好ましいが、これらに限定されるものではない。

【００３２】さらに、ガラス基板の表面状態について、例えばフロートガラスの場合、該ガラスのトップ面とボトム面において明らかに差異があり、フロートガラスの火造り面であるトップ面に被膜することが好ましく、同

様にロールアウト法で製造されるガラスについても、搬送ロール等と接触していない火造り面に被覆することが好ましいが、場合によっては、ボトム面あるいは非火造り面でも被覆できる。撥水性被膜形成用溶液を塗布するガラス基板の表面を予め研摩処理し、酸処理することにより表面改質すると、被膜の強度等が増し好ましいが、その方法は以下のようにして行う。

【００３３】ガラス基板の表面改質のための研摩処理は、錫の混入が少ないフロートガラストップ面、ロールアウトガラス面もしくはこれらの曲げまたは／および強化ガラス面等を、酸化セリウム（セリア）または／および酸化アルミニウム（アルミナ）または／および酸化珪素等の無機金属酸化物を主成分とする微細粉体（平均粒径が約５μｍ以下、好ましくは約１μｍ以下）である表面研摩剤を用い、湿式あるいは乾式でブラシ、スポンジまたは布などの研摩面にて、使用する粉体の種類とその粒径、研摩面の材質およびガラス基板との接触圧などを適宜変えることで、前記ガラス基板面の表面疵状態や研摩状態を制御しつつ研摩することが好ましい。

【００３４】次いで、該研磨処理したガラス面を、塩酸、硫酸、硝酸等の無機酸或いは酢酸、ギ酸もしくは蓚酸等の有機酸を、たとえばｐＨ４濃度以下になるように添加調整した水溶液でなる酸処理液を用い、例えば酸処理液の温度が５℃～７０℃以下、処理時間１０秒～１０分以下の条件下で酸処理することで、研摩処理したガラス表面のナトリウムイオンの抽出やシロキサン結合の切断によりシラノール基を効率的に生成するようにし、該シラノール基が後工程の撥水処理において撥水性フルオロアルキル基の固定化に寄与するものとすることができる。なお酸処理は、酸溶液中に浸漬して行うが、他にスプレー法、フロー法等、浸漬法と同等あるいは近似した酸処理効果が得られる方法であれば特に限定するものではなく採用できる。

【００３５】またさらに、ガラス基板への膜付け法としては、手塗り（ラビング法）、ノズルフローコート法、ディッピング法、スプレー法、リバースコート法、フレキソ法、印刷法、フローコート法あるいはスピンコート法、ならびにそれらの併用等既知の塗布手段、さらに本出願人が出願提案した各種塗布法等が適宜採用し得るものである。また、成膜後の熱処理条件としては、例えば８０℃以上３５０℃以下で１分間乃至６０分間のキュアリングを行い成膜するのが好ましい。

【００３６】

【作用】本発明は、撥水性被膜形成用溶液の加水分解および重縮合反応を制御することにより、主成分として単量体のみを形成するようした撥水性被膜形成用溶液とし、制御した被覆環境下で基材表面に被覆し薄膜を成膜することにより、撥水剤成分と基材表面との反応性が効率化され、基材表面にフルオロアルキル基の高密度化された単分子層を形成することが可能となる。得られた撥水性膜は、格段に優れた耐摩耗性を有し、高硬度かつ高密着性であって耐久性を併せ持ち、より長期的に優れた撥水性能、例えば接触角が約９０°程度以上を維持することができる。

【００３７】

【実施例】以下、実施例により本発明を具体的に説明する。但し、本発明は係る実施例に限定されるものではない。

【００３８】実施例１

撥水性被膜形成用溶液の調合は以下のようにして行った。撥水性被膜を形成するための撥水性被膜形成用溶液組成の原料として、フルオロアルキルトリイソプロポキシシラン〔$CF_3(CF_2)_7CH_2CH_2Si(OC_3H_7)_3$（以下、「ＦＡＳ－Ｐ」と略す）；東芝シリコーン製ＸＣ９５-Ａ９７１５〕と、希釈溶媒に、用いる撥水剤のアルコキシ基の種類と等しいアルコールであるイソプロピルアルコール〔（以下、「ｉ－ＰＡ」と略す）；キシダ化学製〕と、酸触媒である０．１Ｎ－硝酸〔キシダ化学製〕を用い、その配合割合をＦＡＳ－Ｐ：ｉ－ＰＡ：Ｏ．１Ｎ－HNO_3＝１：１２.５：０．３（単位：ｇ）とし、室温で約２時間撹拌し加水分解反応を行い、撥水性被膜形成用溶液を調製した。

【００３９】この溶液中のＦＡＳにおける単量体の存在割合を測定した結果、表１に示すように単量体は９９．５重量%、２量体は０．５重量%、３量体は０重量%であった。なお、重合度の測定は以下の方法により行った。

〔重合度測定〕

測定方法	：ゲルパーミューエーションクロマトグラフィー法（以下、「ＧＰＣ」と略す）
測定機器	：高速ＧＰＣ装置ＨＬＣ-８０２０（東ソー製）
カラム	：ＴＳＫｇｅｌＧ４０００Ｈ-ＨＲ、Ｇ３０００Ｈ-ＨＲ、Ｇ２０００Ｈ-ＨＲおよびＧ２０００Ｈ-ＨＲ（何れも東ソー製）の４つのカラム（各３０ｃｍ）を直列に繋いだもの（カラムの温度は、４０℃に保持）
検出器	：示差屈折計（検出器の温度は、３８℃に保持）
溶出液	：テトラヒドロフラン

（流量は１１／分）
撥水性被膜形成用溶液の注入量　：５０μｌ

なお、ＧＰＣ測定用の撥水性被膜形成用溶液試料は、シラノール基を不活性化し、さらに溶出液との屈折率差をより大きくするために、ＴＭＳ（トリメチルシリル）化剤の一つである、トリメチルクロロシラン（（ＣＨ3)3ＳｉＣｌ：ＴＭＣＳ）を用いて、該溶液中のＦＡＳの加水分解物および重縮合物をＴＭＳ化したのち、孔径０．５μｍのフィルターで試料（撥水性被膜形成用溶液）をろ過した。ＴＭＳ化のための反応条件は、５ｇの試料（撥水性被膜形成用溶液）に対し、０．５７ｇのＴＭＣＳを加えて、室温で１ｈ撹拌した。得られたＧＰＣチャートにおける各ピークから、脱水撥水性被膜形成用溶液中にはＦＡＳの単量体（Ｍｏｎｏｍｅｒ）、２量体（Ｄｉｍｅｒ）および３量体（Ｔｒｉｍｅｒ）の保持時間を、３２.５、３０.８および２９.９分と同定できた。

【００４０】また、それぞれの重合体の存在比は、ピーク面積の比により求めた。（但し、単量体、２量体および３量体のＴＭＳ化合物の屈折率は変化しないと仮定した）。

【００４１】続いて、基材表面への撥水性被膜の形成は以下のようにして行った。２００㎜×３００㎜×３.５㎜ｔサイズのフロートガラス基板の表面を、研摩液とブラシポリッシャーを用いて研摩後、十分に研摩剤を除去し、３５℃の０.１Ｎ硫酸水溶液中に１分間浸漬した。その後、市販のガラス洗浄機にて水洗および乾燥して、温度と湿度を２３℃，４５％ＲＨに保った環境下で、ガラス基板１枚当たり２ｍｌ／枚の撥水性被膜形成用溶液を滴下し、綿布（商品名ベンコット）でガラス全面に十分引き伸ばした後、５分間程度風乾した。続いて、マッフル炉内にガラス基板を投入し、該ガラス基板の温度が５分間で１４０℃に達するような熱処理（以下、キュアリングと呼ぶ）を行ったのち炉内より取出し、ガラス基板表面に白濁して残っている余剰な撥水剤をｉ－ＰＡを含ませた綿布で拭き上げて透明な撥水性ガラス基板を得た。なお、上記の研摩液は、ミレーク(A+B)（三井金属工業製）：水＝１：１００（重量％）なる懸濁液を用いた。

【００４２】得られた撥水性被膜付きガラスの初期接触角は１０８°と高い撥水性を示した。なお、撥水性試験は次の方法により評価した。

【００４３】

〔撥水性試験〕

測定機器	：協和界面科学製ＣＡ－Ｘ２００型
測定環境	：大気中（約２５℃）
水	：純水（２μｌ）の水滴
評価	：ガラス面上に上記の水滴を落とし、該ガラスと水滴のなす角度（°）（すなわち、接触角と呼ぶ）を測定した。

【００４４】実施例２

実施例１と比較して、撥水剤の濃度を低め、原料の配合割合をＦＡＳ－Ｐ：ｉ－ＰＡ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例１と同じで行った。

【００４５】結果、表１に示すように、単量体の存在割合は９９.９重量％、２量体は０.１重量％、３量体は０であり、ほぼ単量体のみからなる撥水性被膜形成用溶液を得ることができた。なお、得られた撥水性被膜付きガラスの耐トラバース性を測定した結果、９３～１０５°と安定して高い値が得られ、良好であった。なお、耐トラバース性は下記の方法にて評価した。

【００４６】

〔耐摩耗性試験〕

試験機	：トラバース式摺動試験機（当社製作機）
試料サイズ	：約２００ｍｍ×３００ｍｍ
摩擦布への荷重	：キャンバス布に０．１ｋｇ／ｃｍ²（ＪＩＳ　Ｌ３１０２－１２０６）
ストローク	：１００ｍｍの往復摺動（摺動回数は往復の回数）
摺動速度	：３０往復／分
評価	：摺動回数３５００回後の接触角θ（°）の測定。

【００４７】実施例３

実施例１と比較して、撥水剤の濃度を低め、原料の配合割合をＦＡＳ－Ｐ：ｉ－ＰＡ：０．１Ｎ－ＨＮＯ３＝１：５０：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例１と同じで行った。

【００４８】結果、表１に示すように、単量体の存在割合は９９.９重量％、２量体は０.１重量％、３量体は０であり、ほぼ単量体のみからなる撥水性被膜形成用溶液を得ることができた。

【００４９】実施例４

実施例１と比較して、撥水剤の濃度を低め、原料の配合割合をＦＡＳ－Ｐ：ｉ－ＰＡ：０．１Ｎ－ＨＮＯ３＝

１：７５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例１と同じで行った。

【００５０】結果、表１に示すように、単量体の存在割合は９９．９重量％、２量体は０．１重量％、３量体は０であり、ほぼ単量体のみからなる撥水性被膜形成用溶液を得ることができた。

【００５１】実施例５

実施例１と比較して、撥水剤としてフルオロアルキルトリメトキシシラン〔$CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$（以下、「ＦＡＳ-Ｍ」と略す）、信越化学製ＫＢＭ-７８０３〕と、希釈溶媒に、用いる撥水剤のアルコキシ基の種類と等しいアルコールであるメタノール〔（以下、「ＭｅＯＨ」と略す）；キシダ化学製〕と、酸触媒である０．１Ｎ－硝酸〔キシダ化学製〕を用い、その配合割合をＦＡＳ－Ｍ：ＭｅＯＨ：０．１Ｎ－ＨＮＯ3＝１：２５：０．３（単位：ｇ）とし、室温で約２時間撹拌し加水分解反応を行った。なお、その他の条件は、実施例１と同じで行った。

【００５２】結果、表１に示すように、単量体の存在割合は９９．５重量％、２量体は０．５重量％、３量体は０であり、ほぼ単量体のみからなる撥水性被膜形成用溶液を得ることができた。

【００５３】比較例１

実施例１と比較して、撥水剤の濃度を高め、原料の配合割合をＦＡＳ－Ｐ：ｉ－ＰＡ：０．１Ｎ－ＨＮＯ３＝１：５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例１と同じで行った。

【００５４】結果、表１に示すように、単量体の存在割合は９８．７重量％、２量体は１．３重量％、３量体は０であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００５５】図１に上記実施例１～４および比較例１の撥水性被膜形成用溶液をＴＭＳ化後に測定したＧＰＣチャートを示す。結果、撥水性被膜形成用溶液中の撥水剤の濃度が１５重量％以下である実施例１～４には２量体のピークが殆ど現れていないのに対して、該濃度が１５重量％以上である比較例１は２量体のピークが明らかに現れている。なお、図中の①は実施例１、②は実施例２、③は実施例３、④は実施例４および⑤は比較例１にそれぞれ対応する曲線を示す。

【００５６】比較例２

実施例２と比較して、希釈溶媒をメタノールとし、原料の配合割合をＦＡＳ－Ｐ：ＭｅＯＨ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。

【００５７】結果、表１に示すように、単量体の存在割合は９９．０重量％、２量体は１．０重量％、３量体は０であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００５８】比較例３

実施例２と比較して、希釈溶媒をエタノール〔（以下、「ＥｔＯＨ」と略す）；キシダ化学製〕とし、原料の配合割合をＦＡＳ－Ｐ：ＥｔＯＨ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例２と同じで行った。

【００５９】結果、表１に示すように、単量体の存在割合は９９．０重量％、２量体は１．０重量％、３量体は０であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００６０】比較例４

実施例２と比較して、希釈溶媒をｎ-ブタノール〔（以下、「ＢｕＯＨ」と略す）；キシダ化学製〕とし、原料の配合割合をＦＡＳ－Ｐ：ＢｕＯＨ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例２と同じで行った。

【００６１】結果、表１に示すように、単量体の存在割合は９９．０重量％、２量体は１．０重量％、３量体は０であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００６２】図２に実施例２および比較例２～４の撥水性被膜形成用溶液をＴＭＳ化後に測定したＧＰＣチャートを示す。結果、ＦＡＳ－Ｐと同一の溶媒（ｉ－ＰＡ）を用いた実施例２では２量体のピークは殆ど現れていないが、その他の溶媒を用いた比較例２～４では２量体のピークが明らかに現れている。なお、図中の①は実施例２、②は比較例２、③は比較例３および④は比較例４にそれぞれ対応する曲線を示す。

【００６３】比較例５

実施例５と比較して、希釈溶媒をエタノールとし、原料の配合割合をＦＡＳ－Ｍ：ＥｔＯＨ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例５と同じで行った。

【００６４】結果、表１に示すように、単量体の存在割合は９８．６重量％、２量体は１．４重量％、３量体は０であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００６５】比較例６

実施例５と比較して、希釈溶媒をイソプロピルアルコールとし、原料の配合割合をＦＡＳ－Ｍ：ｉ-ＰＡ：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例５と同じで行った。

【００６６】結果、表１に示すように、単量体の存在割合は９８．４重量％、２量体は１．４重量％、３量体は０．２であり、目標の９９．５重量％以上の単量体濃度は得られなかった。なお、耐トラバース性を測定した結果、５０～１００°と不安定な値を示し、好ましいものではなかった。

【００６７】比較例７

実施例５と比較して、希釈溶媒をブタノールとし、原料の配合割合をＦＡＳ－Ｍ：ＢｕＯＨ：０．１Ｎ－ＨＮＯ

３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例５と同じで行った。

【００６８】結果、表１に示すように、単量体の存在割合は９８．５重量％、２量体は１．３重量％、３量体は０．２であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００６９】比較例８

実施例５と比較して、希釈溶媒をアセトンとし、原料の配合割合をＦＡＳ－Ｍ：アセトン：０．１Ｎ－ＨＮＯ３＝１：２５：０．３（単位：ｇ）としたものである。なお、その他の条件は、実施例５と同じで行った。

【００７０】結果、表１に示すように、単量体の存在割合は９０．４重量％、２量体は９．１重量％、３量体は０．５であり、目標の９９．５重量％以上の単量体濃度は得られなかった。

【００７１】比較例９

実施例５と比較して、酸触媒（０．１Ｎ硝酸）を加えない、原料の配合割合をＦＡＳ－Ｍ：ＭｅＯＨ：０．１Ｎ－ＨＮＯ３＝１：２５：０（単位：ｇ）としたものである。なお、その他の条件は、実施例５と同じで行った。

【００７２】結果、表１に示すように、単量体の存在割合は９９．９重量％以上、２量体および３量体は０であったが、初期接触角は９０°と低く、撥水性被膜形成用溶液中では加水分解反応が全く起こっていないものと示唆された。なお、耐トラバース性を測定した結果、６０°以下の値であり、好ましいものではなかった。

【００７３】

【表１】

ｻﾝﾌﾟﾙＮｏ	撥水剤の種類	溶媒の種類	酸触媒の種類	撥水液中の撥水剤濃度（wt%）	撥水液中のFAS重合体含有割合（wt%）		
					３量体	２量体	単量体
実施例１	FAS-P	i-PA	HNO3	7.2	0	0.5	99.5
実施例２	FAS-P	i-PA	HNO3	3.8	0	0.1	99.9
実施例３	FAS-P	i-PA	HNO3	1.9	0	0.1	99.9
実施例４	FAS-P	i-PA	HNO3	1.3	0	0.1	99.9
実施例５	FAS-M	MeOH	HNO3	3.8	0	0.5	99.5
比較例１	FAS P	i-PA	HNO3	15.9	0	1.3	98.7
比較例２	FAS-P	MeOH	HNO3	3.8	0	1.0	99.0
比較例３	FAS-P	EtOH	HNO3	3.8	0	1.0	99.0
比較例４	FAS-P	BuOH	HNO3	3.8	0	1.0	99.0
比較例５	FAS-M	EtOH	HNO3	3.8	0	1.4	98.6
比較例６	FAS-M	i-PA	HNO3	3.8	0.2	1.4	98.4
比較例７	FAS-M	BuOH	HNO3	3.8	0.2	1.3	98.5
比較例８	FAS-M	アセトン	HNO3	3.8	0.5	9.1	90.4
比較例９	FAS-M	MeOH	なし	3.8	0	0	＞99.9

【００７４】

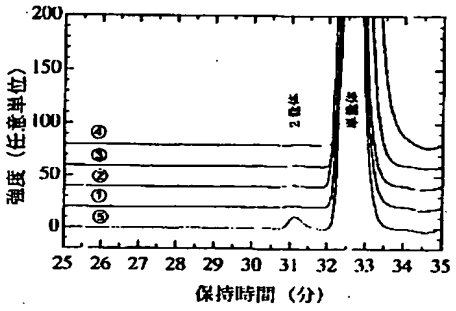
【発明の効果】以上前述したように、本発明によれば、極めて優れた耐摩耗性（耐トラバース性）を示し、量産下で安定かつ確実に優れた撥水性能を維持し耐久性が高いガラス等の撥水性基材が、簡便に効率よく得られ、品質の均質化を向上し、光学特性を損なうことがないので、建築用はもとより自動車用窓材、船舶や航空機の窓材、浴室用あるいは自動車用などのミラー、産業用ガラス等各種の物品に広く採用できる利用価値の高い、有用な撥水性被膜形成用溶液を提供することができる。

【図面の簡単な説明】

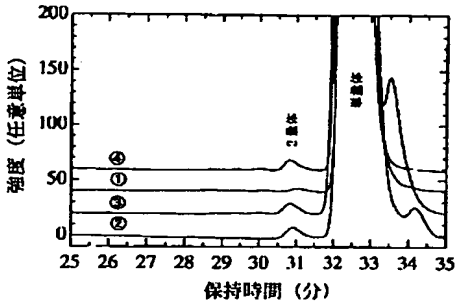
【図１】撥水性被膜形成用溶液のＧＰＣチャート

【図２】撥水性被膜形成用溶液のＧＰＣチャート

【図1】


200
150
100
50
0
強度（任意単位）
25 26 27 28 29 30 31 32 33 34 35
保持時間（分）
2量体
単量体
④
③
②
①
⑤

【図2】


200
150
100
50
0
強度（任意単位）
25 26 27 28 29 30 31 32 33 34 35
保持時間（分）
2量体
単量体
④
①
③
②

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☒ BLACK BORDERS
- ☒ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLORED OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REPERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.
As rescanning documents *will not* correct images problems checked, please do not report the problems to the IFW Image Problem Mailbox